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Carbon Nanotubes

Synthesis, Structure, Properties, and Applications

With 235 Figures

Springer

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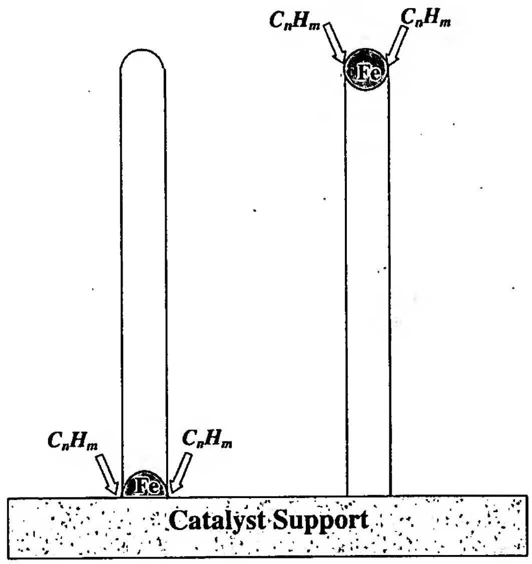

Fig. 3. Two general growth modes of nanotube in chemical vapor deposition. *Left diagram:* base growth mode. *Right diagram:* tip growth mode

cobalt and nickel are also the favored catalytic metals used in laser ablation and arc-discharge. This simple fact may hint that the laser, discharge and CVD growth methods may share a common nanotube growth mechanism, although very different approaches are used to provide carbon feedstock.

A major pitfall for CVD grown MWNTs has been the high defect densities in their structures. The defective nature of CVD grown MWNTs remains to be thoroughly understood, but is most likely be due to the relatively low growth temperature, which does not provide sufficient thermal energy to anneal nanotubes into perfectly crystalline structures. Growing perfect MWNTs by CVD remains a challenge to this day.

1.2.2 Single-Walled Nanotube Growth and Optimization

For a long time, arc-discharge and laser-ablation have been the principal methods for obtaining nearly perfect single-walled nanotube materials. There are several issues concerning these approaches. First, both methods rely on evaporating carbon atoms from solid carbon sources at $\geq$ 3000°C, which is not efficient and limits the scale-up of SWNTs. Secondly, the nanotubes synthesized by the evaporation methods are in tangled forms that are difficult to purify, manipulate and assemble for building addressable nanotube structures.

Recently, growth of single-walled carbon nanotubes with structural perfection was enabled by CVD methods. For an example, we found that by using methane as carbon feedstock, reaction temperatures in the range of 850–1000°C, suitable catalyst materials and flow conditions one can grow high quality SWNT materials by a simple CVD process [20,21,22,23]. High tem-

perature is necessary to form SWNTs that have small diameters and thus high strain energies, and allow for nearly-defect free crystalline nanotube structures. Among all hydrocarbon molecules, methane is the most stable at high temperatures against self-decomposition. Therefore, catalytic decomposition of methane by the transition-metal catalyst particles can be the dominant process in SWNT growth. The choice of carbon feedstock is thus one of the key elements to the growth of high quality SWNTs containing no defects and amorphous carbon over-coating. Another CVD approach to SWNTs was reported by Smalley and coworkers who used ethylene as carbon feedstock and growth temperature around 800°C [24]. In this case, low partial-pressure ethylene was employed in order to reduce amorphous carbon formation due to self-pyrolysis/dissociation of ethylene at the high growth temperature.

Gaining an understanding of the chemistry involved in the catalyst and nanotube growth process is critical to enable materials scale-up by CVD [22]. The choice of many of the parameters in CVD requires to be rationalized in order to optimize the materials growth. Within the methane CVD approach for SWNT growth, we have found that the chemical and textural properties of the catalyst materials dictate the yield and quality of SWNTs. This understanding has allowed optimization of the catalyst material and thus the synthesis of bulk quantities of high yield and quality SWNTs [22]. We have developed a catalyst consisting of Fe/Mo bimetallic species supported on a sol-gel derived alumina-silica multicomponent material. The catalyst exhibits a surface are of approximately 200 m^2/g and mesopore volume of 0.8 mL/g. Shown in Fig. 4 are Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) images of SWNTs synthesized with bulk amounts of this catalyst under a typical methane CVD growth conditions for 15 min (methane flow rate = 1000 mL/min through a 1 inch quartz tube reactor heated to 900°C). The data illustrates remarkable abundance of individual and bundled SWNTs. Evident from the TEM image is that the nanotubes are free of amorphous carbon coating throughout their lengths. The diameters of the SWNTs are dispersed in the range of 0.7–3 nm with a peak at 1.7 nm. Weight gain studies found that the yield of nanotubes is up to 45 wt.% (1 gram of catalyst yields 0.45 gram of SWNT).

Catalyst optimization is based on the finding that a good catalyst material for SWNT synthesis should exhibit strong metal-support interactions, possess a high surface area and large pore volume. Moreover, these textural characteristics should remain intact at high temperatures without being sintered [22]. Also, it is found that alumina materials are generally far superior catalyst supports than silica. The strong metal-support interactions allow high metal dispersion and thus a high density of catalytic sites. The interactions prevent metal-species from aggregating and forming unwanted large particles that could yield to graphitic particles or defective multi-walled tube structures. High surface area and large pore volume of the catalyst support facilitate high-yield SWNT growth, owing to high densities of catalytic sites

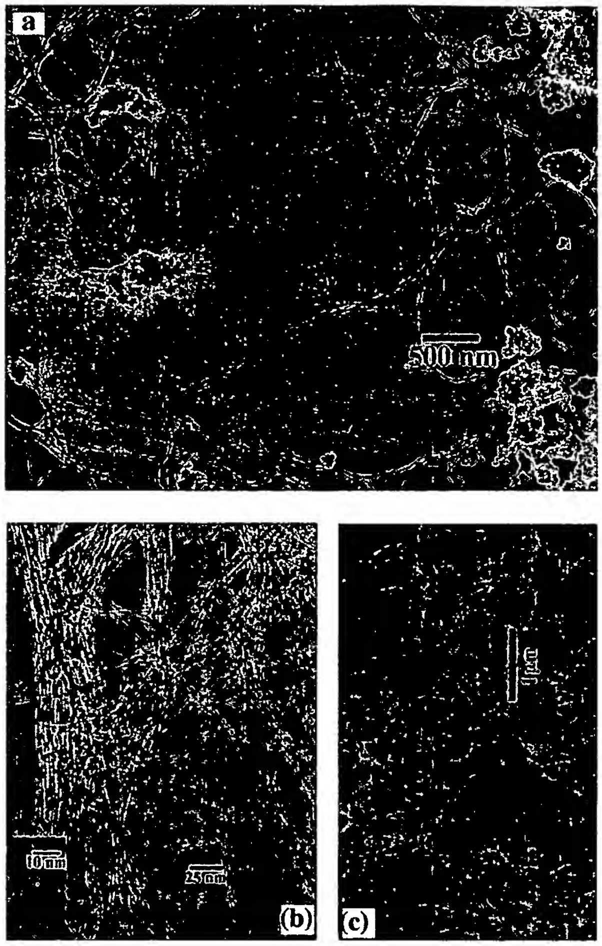

Fig. 4. Bulk SWNT materials grown by chemical vapor deposition of methane. (**a**) A low magnification TEM image. (**b**) A high magnification TEM image. (**c**) An SEM image of the as-grown material

made possible by the former and rapid diffusion and efficient supply of carbon feedstock to the catalytic sites by the latter.

Mass-spectral study of the effluent of the methane CVD system has been carried out in order to investigate the molecular species involved in the nanotube growth process [25]. Under the typical high temperature CVD growth condition, mass-spectral data (Fig. 1.2.2) reveals that the effluent consists of mostly methane, with small concentrations of H_2, C_2 and C_3 hydrocarbon species also detected. However, measurements made with the methane source at room temperature also reveals similar concentrations of H_2 and C_2–C_3 species as in the effluent of the 900°C CVD system. This suggests that the H_2 and C_2–C_3 species detected in the CVD effluent are due to impurities in the methane source being used. Methane in fact undergoes negligible self-pyrolysis under typical SWNT growth conditions. Otherwise, one would

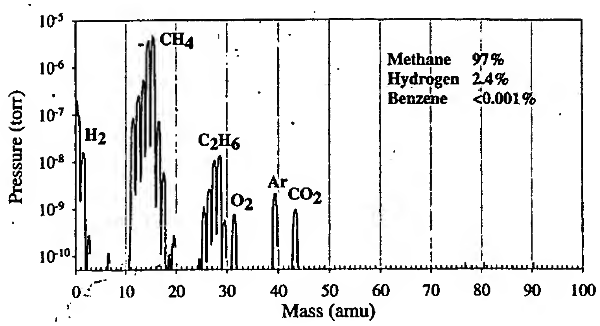

Fig. 5. Mass spectrum recorded with the effluent of the methane CVD system at 900°C

observe appreciable amounts of H_2 and higher hydrocarbons due to methane decomposition and reactions between the decomposed species. This result is consistent with the observation that the SWNTs produced by methane CVD under suitable conditions are free of amorphous carbon over-coating.

The methane CVD approach is promising for enabling scale-up of defect-free nanotube materials to the kilogram or even ton level. A challenge ist wheter it is possible to enable 1 g of catalyst producing 10, 100 g or even more SWNTs. To address this question, one needs to rationally design and create new types of catalyst materials with exceptional catalytic activities, large number of obtain active catalytic sites for nanotube nucleation with a given amount of catalyst, and learn how to grow nanotubes continuously into macroscopic lengths.

A significant progress was made recently by *Liu* and coworkers in obtaining a highly active catalyst for methane CVD growth of SWNTs [26]. Liu used sol-gel synthesis and supercritical drying to produce a Fe/Mo catalyst supported on alumina aerogel. The catalyst exhibits an ultra-high surface area ($\sim$ 540 m^2/g) and large mesopore volume ($\sim$ 1.4 mL/g), as a result of supercritical drying in preparing the catalyst. Under supercritical conditions, capillary forces that tend to collapse pore structures are absent as liquid and gas phases are indistinguishable under high pressure. Using the aerogel catalyst, Liu and coworkers were able to obtain $\sim$ 200% yield (1 g of catalyst yielding 2 g of SWNTs) of high quality nanotubes by methane CVD. Evidently, this is a substantial improvement over previous results, and is an excellent demonstration that understanding and optimization of the catalyst can lead to scale-up of perfect SWNT materials by CVD.

The growth of bulk amounts of SWNT materials by methane CVD has been pursued by several groups. *Rao* and coworkers used a catalyst based on mixed oxide spinels to growth SWNTs [27]. The authors found that good quality and yield of nanotubes were obtainable with FeCo alloy nanoparticles. Colomer and coworkers recently reported the growth of bulk quantities of SWNTs by CVD of methane using a cobalt catalyst supported on magnesium oxide [28]. They also found that the produced SWNTs can be separated from the support material by acidic treatment to yield a product with about 70–80% of SWNTs.